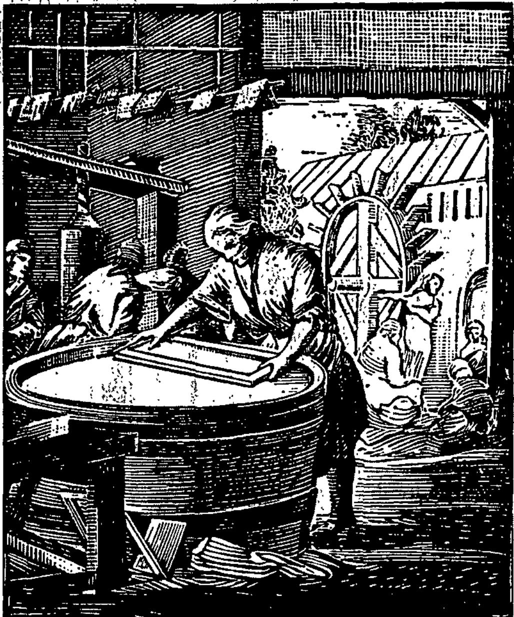

INSTITUTE OF PAPER CHEMISTRY
Appleton · Wisconsin

MOLECULAR STRUCTURE OF LIGNOSULFONATES

MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Thirteen

A Progress Report

to

ENVIRONMENTAL RESEARCH GROUP

June 8, 1971

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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MOLECULAR STRUCTURE OF LIGNOSULFONATES
MECHANICAL AND ADHESIONAL BEHAVIOR

SUMMARY

This is Progress Report Thirteen of Project 2421 entitled "Investigation of the Relationship Between Lignin Structure and its Mechanical and Adhesional Behavior." The focus of the work is primarily on plywood applications, and it has been shown that the surface tension and viscomechanical properties of lignosulfonates are similar to good phenol-formaldehyde adhesives indicating that they have good potential. A major weakness of lignosulfonate adhesive is low cohesive strength, which can be overcome by increasing chemical cross-linking as measured by the amount of water insolubility achieved. The work herein reported describes the effect of concentration, temperature and time on the insolubility achieved in the lignosulfonic acid — Catalin system, the most successful lignosulfonate plywood adhesive to date, with the objective of optimizing the reaction.

The parameter variations were as follows: lignosulfonic acid concentration (15-45%), Catalin concentration (0-50% with respect to lignosulfonate), temperature (275-345°F.), and time (3-6 min.). The selected adhesive was added to a glass fiber mat, pressed to 28 p.s.i., cured under the prescribed conditions, and extracted with boiling water for three hours, as described in previous work.

The most important parameters to achieve water insolubility are lignosulfonate concentration and temperature, followed by Catalin concentration, and finally press time. About 60% water insolubility is achieved under conditions equivalent to the currently formulated adhesive (27% ELSA, 40% Catalin, 300°F., and 4 min.). This can be increased to 90-95% insolubility by increasing ELSA concentration and temperature, or temperature and time. In general, the higher the ELSA

concentration the lower the Catalin concentration required to achieve a given water insolubility for a given temperature and time. An insolubility of 80% was achieved with only 5% Catalin at 45% ELSA, 345°F. and 5 min. This is a most significant lead in adhesive formulation, since Catalin is the most expensive component of the system.

Catalin systems with calcium or ammonium-base spent sulfite liquors, acidified to the same pH as the electrodialyzed material, gave insolubility reactions equivalent to the Catalin-ELSA system. The low pH is the significant property of ELSA and not the electrodialysis *per se*.

The next stage in the experimental program is to test adhesive formulations and conditions selected from above for plywood bonding behavior. Insolubilities will also be determined for cross-linking reactions of lignosulfonate and formaldehyde sources with and without added phenolics at low pH, and of lignosulfonate and diepoxides at high pH. The most promising combinations will be tested for bonding in particle board and in road aggregates.

INTRODUCTION

This is Progress Report Thirteen of Project 2421 entitled "Investigation of the Relationships Between Lignin Structure and its Mechanical and Adhesional Behavior." The focus of the project has been on the adhesional and mechanical behavior of lignosulfonate adhesives, and their relationships to adhesive [illegible] strength, particularly in plywood operations. The surface tension and [illegible] properties of lignosulfonates were found to be similar to good adhesives, such as phenol-formaldehyde, indicating that they have good adhesive potential. Penetration of the adhesive into the porous wood surface was found to be an important limitation of the strength of the adhesive bond in the plywood. Hse (1) reached the same conclusion in a recent paper. The low cohesive strength of the lignosulfonate adhesives is a major limitation in their use and it has been shown that the development of cross-linking in these adhesives, as measured by water insolubility, greatly improves their bonding strength (2). Hse (1) likewise found good [illegible] development with resins of high reactivity and suggests that this appears to be due to the production of a high degree of cross-linking.

The present work explores the effects of Catalin and lignosulfonate concentrations, temperature, time, and, to some extent, lignosulfonate type on the development of water insolubility of the cured adhesive. Such data provide the foundation for optimizing the lignosulfonic acid adhesive formulation for use in bonding plywood.

EXPERIMENTAL

PREPARATION OF CURED ADHESIVES

The cured adhesives were prepared as previously described (2). Five glass fiber filter pads (5.5 cm. in diameter), previously conditioned and weighed, were saturated with the lignosulfonate preparation, placed on silicon-treated aluminum foil, and put in the heated press as described in Progress Report Eleven (3) at 28 p.s.i. for the prescribed temperature and time. After conditioning the disks again to 73°F. and 50% R.H., one of them was removed, weighed and placed in the cotton bag for the boil test. After the bag was tied shut, the free strings were cut off to avoid subsequent entanglement.

WATER SOLUBILITY OF THE CURED ADHESIVES

The cured adhesive disks in the bags were subjected to boiling water extraction for three hours in a steam heated round-bottom flask with overflow as previously described (2). At the end of the boil period, the bags were removed from the flask and allowed to dry at 73°F. and 50% R.H. at least overnight. All of the remaining pieces of disk were carefully removed and weighed. If more drying time was needed, the pieces were allowed to dry to a constant weight.

The percentage of adhesive insolubility was calculated from the weights of the disk without adhesive, before boil and after boil.

RESULTS AND DISCUSSION

ELECTRODIALYZED LIGNOSULFONIC ACID — CATALIN ADHESIVE

A quantity of electrodialyzed ammonium base lignosulfonate (R-1 70-56 2985 No. 7) was prepared for the Finnish Bark Board Association and for use in these studies. A sample of this was used to make a batch of formulated adhesive and a set of ten Southern pine plywood panels was made and tested as previously described (4) (see Appendix I). The average bond strength in shear was 212 ± 20 lb./sq.in. and the failure was 50-90% in the wood. This agrees reasonably well with other ELSA samples tested and this material is considered to be typical of electrodialyzed lignosulfonates.

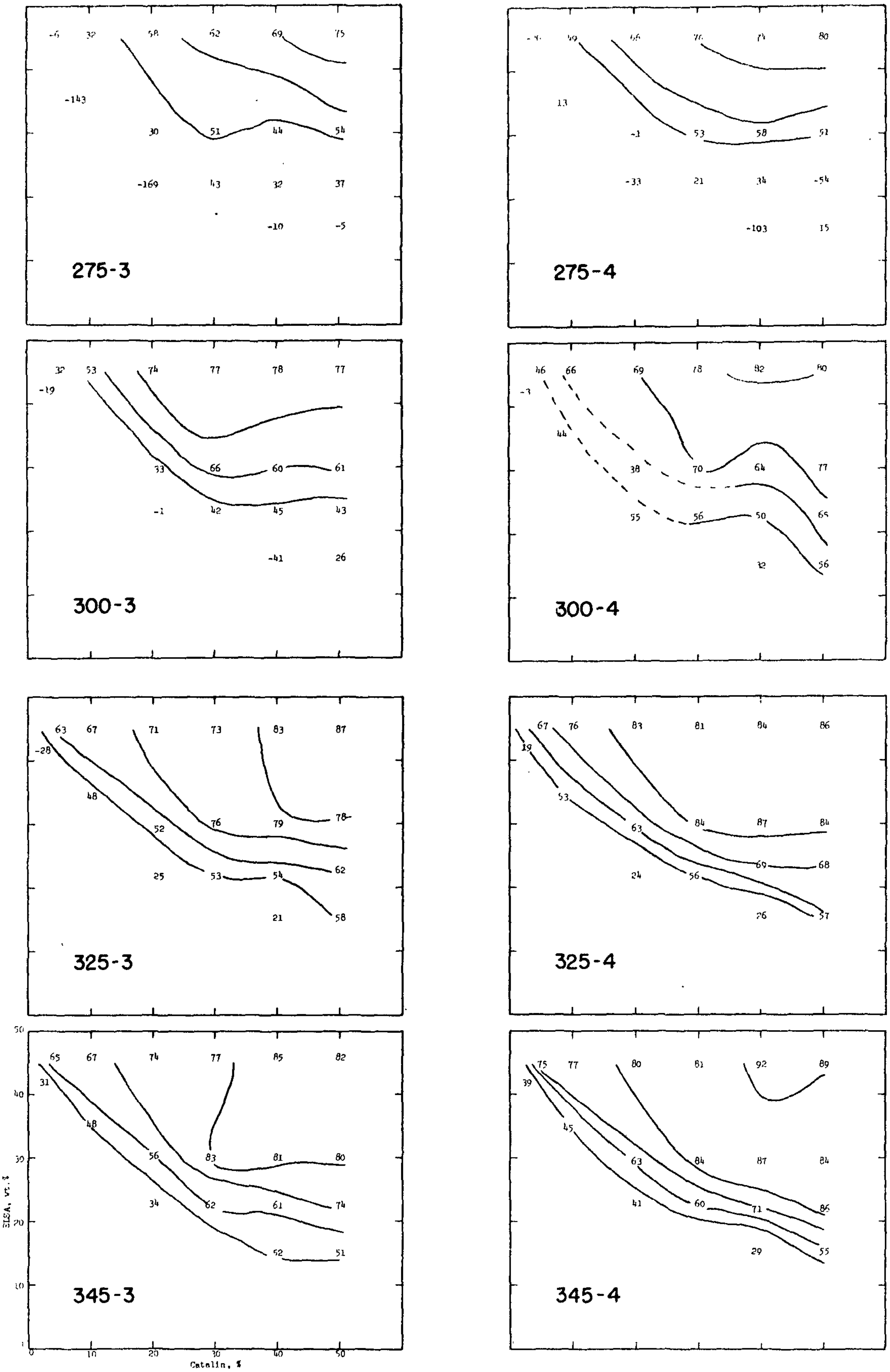
Using glass fiber, adhesive-impregnated disks, as previously described (3), the variables ELSA concentration (15-45%), Catalin (CR-9357, Ashland Chemical Company, Chicago, Ill.) concentration (0-50% with respect to the ELSA solids), platen temperature (275-345°F.), and press time (3-6 min.), were studied using boiling water insolubility as the measured property. The pressing force was held constant at 28 p.s.i. and even at this low pressure many of the disks spread or separated but they still remained identifiable. The results are listed in Table I and the primary data are given in Appendix II. (To prepare the 45% ELSA, the original 42% ELSA was first freeze dried then redissolved.) The "negative" insolubilities result because of the loss of glass fibers from the mat when an adhesive with low insolubility is extracted. For every adhesive studied the first condition (275°F., 4 min.) was repeated at the end of each temperature-time series to check the extent of adhesive change which might have occurred during this time (about two hours). There is no significant change evident. A graphical presentation of these results is given in the composite Fig. 1 which contains plots of

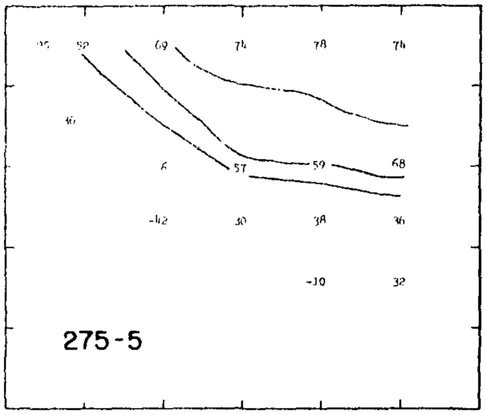
TABLE I

WATER INSOLUBILITY (WT.%) OF ELECTRODIALYZED LIGNOSULFONIC ACID – CATALIN ADHESIVES AS A FUNCTION OF THE CURING TEMPERATURE AND TIME

ELSA Concn.		15		22				30				35	41.6	42	45						
Catalin Concn.		40	50	20	30	40	50	20	30	40	50	8.6	2.5	0	0	5	10	20	30	40	50
Temp., °F.	Time, min.																				
275	3	-10	-5	-169	4	32	37	30	51	44	54	-143	--	--	--	-6	32	58	62	69	75
	4	-103	15	-33	21	34	-54,-12	1,-3	53	58	51	13	--	--	--	-26	49	66	70	74	80
	5	-10	32	-42	30	38	36	7,4	57	59	68	36	--	--	--	25	52	69	74	78	74
	6	38	41	38	16,32	45	44	46	47	54	54	28	--	--	--	26	46	74	78	77	81
300	3	-41	26	-1	42	45	43	33	66	60	61	17	-19	--	--	32	53	74	77,73	78	77
	4	32	56	55	56	50	65	38	70	64	77	44	3	--	--	46	66	69	78	82	80
	5	40	54	32	56	51	72	55	77	71	80	47	11	--	--	58	68	76	75	84	82
	6	34	51	37	60	68	74	59	80	77	75	44	-1	--	--	58	73	76	85	87	89
325	3	21	58	25	53	54	62	52	76	79	78	48	-20	--	--	63	67	71	73	85	87
	4	26	57	24	56	69	68	41	77	80	81	53	19	--	--	67	76	83	81	84	86
	5	30	58	36	63	61	81	53	83	78	82	60	31	--	--	68	82	85	81	88	87
	6	29	69	35	71	65	80	63	86	83	81	52	35	--	--	82	83	87	85	91	93
345	3	52	51	34	62	61	74	56	83	81	80	48	31	--	--	65	67	74	77	85	82
	4	29	55	41	60	71	86	63	84	87	84	45	39	--	--	75	77	80	81	92	89
	5	49	69	36	68	80	87	76	87	84	88	58	44	--	--	80	87	90	88	93	92,91
	6	44	69	70	68	83	90	70	90	90	89	60	48	-25	22	83	89	93	84,85	93	95
275	3	-10	0	-130	36	25	61	-68,-56	8	36	59	-62	--	--	--	-27	44	61	66	71	75
pH		1.18	0.92	0.90	0.90	1.00	1.10	0.86	0.99	--	0.80	0.73	0.80	0.45	0.45	0.54	0.52	0.60	0.40	0.40	0.62
Viscy., cp.		4	5	6	6	7	8	10	11	13	20	18	60	68	280	300	450	800	--	1600	1700

Figure 1. Water Insolubility (Wt.%) of ELSA-Catalin Adhesives Cured as Functions of Temperature Time. (Each Plot is Identified by the Temperature in °F. and Time in Min. The Contours Show Insolubility at Levels of 50, 60, 70, 80, and 90 Wt.%.)


275-3
275-4
300-3
300-4
325-3
325-4
345-3
345-4
Catalin, %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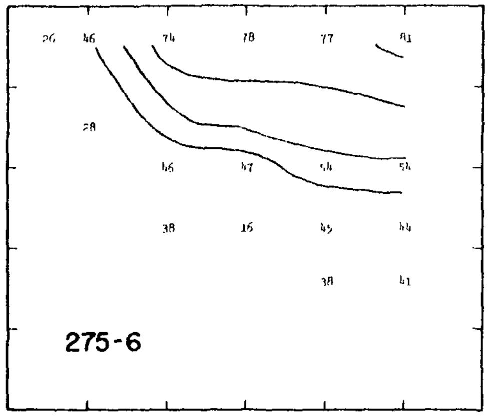
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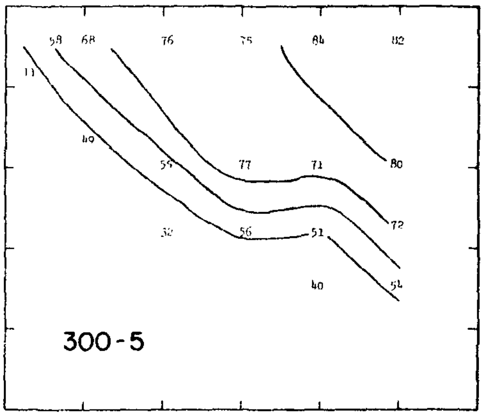
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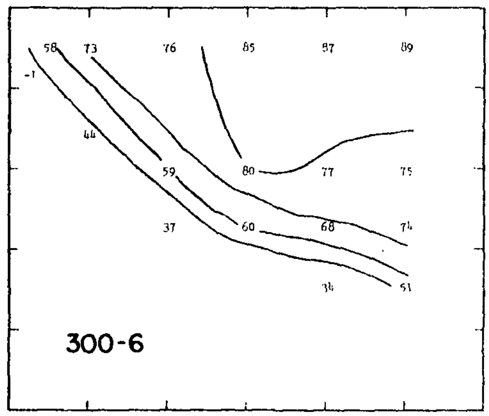
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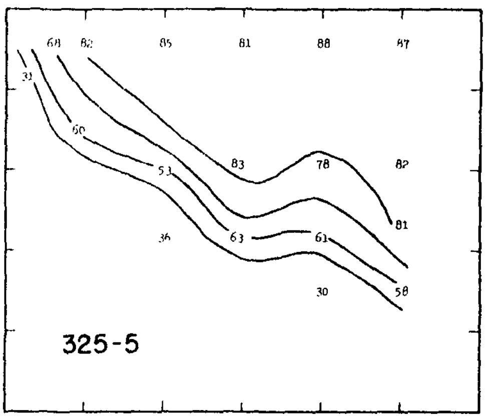
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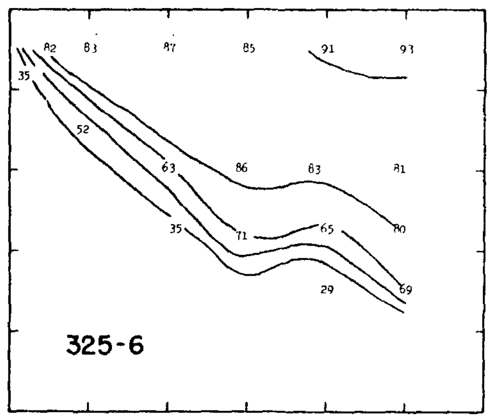
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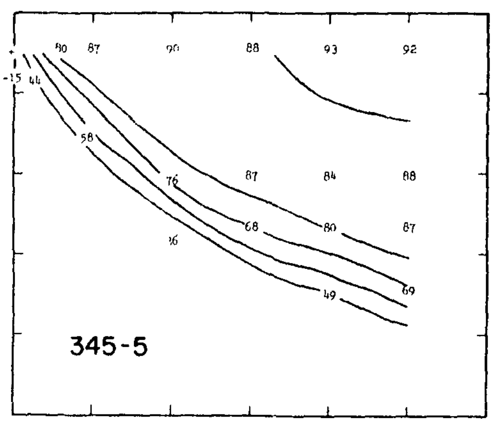
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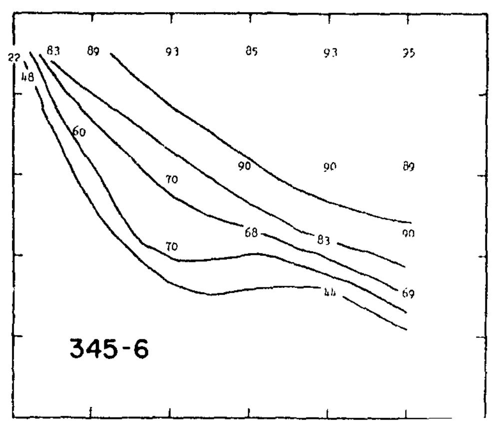
345-6

boiling water insolubility as functions of ELSA concentration and of Catalin concentration for the specified curing condition of temperature and time. Contours of 50, 60, 70, 80, and 90% insolubility are drawn.

The formulated adhesive as currently used is 27% ELSA and 40% Catalin cured at 300°F. for 4 min. This achieves about 60% insolubility according to the above results. It is interesting to note that this essentially agrees with the previously (2) measured insolubility of the formulated adhesive. The insolubility of this adhesive, including the wood meal component, was 89%, which is equivalent to 56% insolubility for the ELSA and Catalin solids assuming that only the ELSA component contributes to the water solubility. If the functional relationship between insolubility and adhesive bond strength previously observed (2) is of general validity for the lignosulfonates, it is then reasoned that the 60% insolubility of these ELSA — Catalin systems represents a threshold of acceptability for plywood adhesive and the higher values may represent improvement.

The variable of major importance is seen to be the concentration of ELSA. As this concentration is increased from 30 to 45% the minimum amount of Catalin needed decreases from about 30% to something less than 5%. This concentration behavior is probably effective by causing a change in the temperature-time history, the higher the concentration the faster is the rise in temperature, as every adhesive eventually achieves a state of "dryness" during the curing time. The reduction of the Catalin ratio may be an important economic factor. This reduction is also fortunate as the viscosity remains reasonable with increasing ELSA when the Catalin is reduced simultaneously. When the Catalin concentration is expressed as an absolute concentration based on the quantity of water present, the functional behavior is similar to those presented but the contours are much more compressed with respect to each other and, thus, no additional insight is evident.

The next most important variable is the curing temperature. Note how the insolubility contours, particularly above [illegible], move to lower ELSA concentrations and to some extent to lower Catalin concentrations, particularly for the high ELSA concentration, as the temperature is increased for a given curing time. The largest increase occurs in going from [illegible] to [illegible] but significant increases continue up to the final temperature surveyed, [illegible].

Finally, the time of curing does affect the degree of insolubility achieved. The largest increase occurs between three and four minutes, which probably still reflects the time for temperature build up in the adhesive layer. Between 4 and 5 min. the increase is less and between [illegible] and [illegible] min. the increase is least and may even be a slight decrease at the lower ELSA concentrations. The increase in curing time is most effective at the high ELSA concentration.

In the curing of ELSA adhesives containing a minimum of Catalin, reasonably high insolubility can be achieved by increasing the ELSA concentration, by increasing the temperature, and by increasing the cure time. For example, the 60% insolubility achieved at [illegible] ELSA [illegible] – [illegible]°F. – [illegible] min., conditions approximating those of the formulation [illegible] can be increased to greater than 80% insolubility by raising the [illegible] or at this higher temperature by increasing the ELSA concentration [illegible] the Catalin concentration can be reduced to 5% and greater than [illegible] achieved in 5 min. Assuming that the previously observed [illegible] between insolubility and plywood bonding strength is valid for [illegible] to reduce the Catalin content of the adhesive and [illegible] curing from that of the current formulation.

ADHESIVE QUALITY WITH ACIDIFIED CaSSL AND NH_4SSL

At the request of the Finnish Bark Board Association, a calcium base spent sulfite liquor (CaSSL) was treated with H_2SO_4 to precipitate some $CaSO_4$ and lower the pH to 0.2. A sample of this was tested for its water insolubilization reaction with Catalin. The concentration of CaSSL and of Catalin selected for this test (30 and 40%, respectively) approximate those in the current adhesive formulation and duplicate conditions with the ELSA sample above. In addition, another batch of ammonium-base spent sulfite liquor was electrodialyzed and a sample of this was likewise tested. The results are listed in Table II.

As seen from these data, the insolubility developed with the CaSSL sample was equal to, or greater than, that developed with the first ELSA sample over the curing temperature and times tested. Based on the insolubility-plywood bonding strength relationship and on the good plywood adhesive bond formed with this ELSA in the formulation, the CaSSL sample should give as good bonding results as the ELSA. This finding is encouraging, since a previous (2) trial involving 50% glyoxal with Toranil B-pH-reduced-with-H_2SO_4 and with Toranil free acid indicated the salt was not as reactive at the same low pH ($\sim$ 0.5) as the free acid, although in this case even the free acid is not too reactive with glyoxal (a "negative" insolubility). However, with 40% Catalin the Toranil free acid resulted in 77% insolubility. Perhaps the glyoxal reaction was not a fair evaluation.

To see if an ammonium-base SSL will also be reasonably reactive under the same pH, Catalin, and cure conditions, the NH_4SSL sample used in the electrodialysis was made to pH = 0.3 by the addition of sulfuric acid. A sample of this was formulated and cured as above (40% SSL solids, 40% Catalin, 275-345°F., 4-6 min.). The results are listed in Table II. The insolubilities achieved are equivalent to those of the ELSA and of the CaSSL. It appears that pH is the important parameter for this insolubility reaction and not electrodialysis *per se*. It is expected, thus, that SSL can be used in plywood adhesives formulated with Catalin by merely reducing the pH to less than 1.0.

TABLE II

WATER INSOLUBILITY (WT.%) OF THE LIGNOSULFONATE — 40% CATALIN ADHESIVE USING DIFFERENT LIGNOSULFONATES ACIDIFIED TO pH OF 0.2

Temp., °F.	Time, min.	30% ELSA	30% ELSA (New Batch)	30% CaSSL	40% ELSA	40% NH_4SSL[a]
275	3	44	57	52	--	--
	4	58	59	63	(70)[b]	80
	5	59	66	70	--	--
	6	54	65	72	(70)	79
300	3	60	70	69	--	--
	4	64	73	73	--	--
	5	71	84	82	--	--
	6	77	86	75	--	--
325	3	79	68	78	--	--
	4	80	85	77	--	--
	5	78	89	87	--	--
	6	83	90	89	--	--
345	3	81	75	78	--	--
	4	87	89	79	(90)	92
	5	84	90	91	--	--
	6	90	94	90	(92)	93
275	3	36	61	28	--	--
pH		--	0.62	0.80	--	0.20

[a] Thickened in two hours at room temperature.

[b] Parentheses indicated these values were estimated using the plots given in Fig. 1.

CONCLUSIONS

The water insolubility of cured lignosulfonic acid with Catalin increases with increasing concentration of lignosulfonate, with increasing temperature, and to some extent with increasing reaction time. The quantity of Catalin relative to the lignosulfonate to achieve a given insolubility may be reduced significantly by increasing the lignosulfonate concentration.

Essentially equal degrees of insolubility may be achieved under identical conditions of reaction with Catalin, whether the spent sulfite liquor is electrodialyzed or is reduced to the same pH as electrodialysis by the addition of acid.

FUTURE WORK

The knowledge of insolubility reaction must now be applied to plywood bonding. Adhesives will be formulated based on this knowledge and will be tested in Southern pine plywood layups. The effects of lignosulfonate concentration, Catalin concentration, temperature, and time will be examined and a comparison will be made with the insolubility data.

The reaction of lignosulfonates with other potential cross-linking agents will be examined by the insolubility produced. These reactions may be useful in replacing the Catalin reaction or in raising the pH of the reacting system. At low pH these will be trioxane (a potential formaldehyde source), trioxane with resorcinol and phloroglucinol, and paraldehyde (a formaldehyde source). At high pH reactions involving the diepoxides, 1,2,3,4-diepoxy butane, 1,2,7,8-diepoxy octane, and Epon 812 (Shell Chemical Company).

The most promising above combinations will be employed in making particle board and in binding sand, a difficult component in road aggregate.

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4. Progress Report Nine, Project 2421, p. 15-20, April 25, 1969.

THE INSTITUTE OF PAPER CHEMISTRY

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John W. Swanson

John W. Swanson, Director
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Materials & Systems

APPENDIX I

PLYWOOD BONDING EFFECTIVENESS OF ELSA

The effectiveness of a freshly prepared batch of ELSA, coded R-1 10-56 2985 No. 7, when incorporated in an adhesive formulation was determined. [illegible] formulation was prepared, and layups were prepared and tested as described [illegible] pages 15 to 20 in Report Nine, Project 2421. The Brookfield viscosity at [illegible]°C. was 450 cps. and the pH was 0.32.

The Southern pine veneer used in the layups was aged a minimum of two [illegible] after sanding. The bonding strength data of the test strips as determined [illegible] Amsler tester are given in Table III.

TABLE III

PLYWOOD BONDING STRENGTH, LB./IN.

[illegible]up [illegible]1	Layup No. 2	Layup No. 3	Layup No. 4	Layup No. 5	Layup No. 6	Layup No. 7	Layup No. 8	Layup No. 9	Layup No. 10
[illegible]	218	--	170	168	148	189	197	184	140
[illegible]	227	124	217	171	124	198	249	168	294
[illegible]	261	236	214	252	298	207	212	151	267
[illegible]	278	198	211	182	258	240	181	220	232
[illegible]	--	218	198	117	178	195	238	136	187
[illegible]	228	--	197	116	228	224	188	144	217
[illegible]	183	--	102	257	183	242	186	202	187
[illegible]	257	331	157	247	245	270	203	144	153
[illegible]	234	273	165	358	213	276	219	163	146
[illegible]	258	313	204	163	173	228	249	179	211
[illegible]	238.2	241.9	183.5	203.1	204.8	226.9	212.2	169.1	203.4

APPENDIX II

BASIC DATA FOR THE ADHESIVE WATER INSOLUBILITY

The weight of the cured adhesive in the disk prior to the boiling water extraction is given in Table IV.

TABLE IV

WEIGHT (MG. PER DISK) OF THE CURED ADHESIVE BEFORE THE WATER INSOLUBILITY MEASUREMENT

ELSA Concn.		15		22				30				35	41.6	42	45							30 CaSSL	30 ELSA (new batch)
Catalin Concn.		40	50	20	30	40	50	20	30	40	50	8.6	2.5	0	0	5	10	20	30	40	50	40	40
Temp., °F.	Time, min.																						
275	3	254.5	300.5	65.9	69.2	83.0	82.6	123.8	120.4	130.0	173.0	95.8	145.3	--	182.7	333.1	245.6	452.4	614.4	651.9	755.3	200.6	232.1
	4	32.1	45.4	61.6	79.0	89.0	85.0	134.3	156.5	149.5	128.3	101.4	194.4	--	203.0	269.4	292.9	712.2	599.2	551.3	1117.4	209.7	224.4
	5	38.1	39.6	65.2	70.4	97.5	87.9	122.9	175.0	131.3	170.4	107.8	143.9	--	201.0	303.6	306.2	1519.3	1275.0	769.3	1359.5	197.2	308.4
	6	35.0	33.9	63.2	79.5	103.6	107.4	133.6	104.5	121.6	122.7	140.4	162.2	--	221.5	286.6	267.1	805.9	918.2	896.0	1020.5	217.8	187.2
300	3	29.5	34.2	62.2	73.7	114.0	87.4	116.7	189.6	133.2	142.4	160.9	176.9	--	256.2	297.6	325.7	821.2	943.3	748.5	1328.6	264.6	455.4
	4	33.4	55.8	82.9	92.0	85.0	110.5	121.7	152.4	133.0	205.6	127.6	158.5	--	200.0	320.5	318.4	1414.7	575.6	1539.8	1430.7	173.7	251.2
	5	36.3	42.7	47.5	75.1	89.5	122.0	100.5	188.0	133.1	174.6	138.2	166.3	--	223.0	332.8	393.5	1479.7	1562.2	1629.9	965.6	249.0	627.2
	6	38.3	43.4	51.2	84.1	105.6	126.6	104.2	192.0	155.4	142.0	120.4	156.3	--	228.4	385.0	467.6	1473.0	682.7	1270.4	1354.0	152.5	621.2
325	3	31.7	43.4	61.8	72.5	83.6	112.3	86.5	166.8	163.8	154.2	129.2	155.3	--	235.6	407.1	296.2	1573.2	1642.1	1564.6	694.9	206.0	796.4
	4	38.8	49.8	42.3	64.4	102.5	100.6	63.3	148.0	136.7	165.4	118.5	158.9	--	166.4	384.5	656.0	1304.8	1479.6	1751.6	1556.6	166.7	401.9
	5	37.1	40.1	57.3	73.2	81.8	127.8	68.0	166.2	111.3	165.3	156.5	125.6	--	180.0	366.1	781.1	1232.6	1223.4	1533.5	1959.0	268.4	327.3
	6	35.0	65.5	45.7	86.5	83.5	115.7	109.3	270.2	140.6	160.2	119.5	154.3	--	228.5	545.6	785.1	1133.4	1554.8	1454.1	1822.7	328.3	624.3
345	3	45.1	58.0	48.2	100.5	76.2	114.9	81.9	178.4	163.8	162.0	146.2	175.3	--	163.9	437.7	645.5	1320.1	1529.6	1802.6	1865.3	476.0	350.4
	4	38.2	51.2	57.3	67.8	107.2	214.6	101.9	266.3	259.5	162.6	99.2	147.2	--	272.2	483.4	820.2	1506.3	1257.6	899.0	1500.6	172.0	554.9
	5	42.0	56.6	47.8	95.3	129.1	210.8	150.7	321.8	119.8	172.1	112.4	198.1	--	203.5	631.0	873.1	1323.6	977.3	1745.8	1600.5	323.5	438.8
	6	32.7	44.8	99.6	70.0	148.2	203.7	120.4	379.8	195.4	214.7	135.8	158.5	163.7	270.6	501.2	739.8	1159.3	2311.1	1604.7	1755.3	289.2	571.8
275	3	247.9	202.2	67.9	80.9	93.2	121.1	107.1	168.8	117.8	167.4	135.4	265.0	--	169.9	266.2	388.6	586.5	573.2	683.5	982.6	119.0	288.9